The Photochemical Rearrangements of Some Photochromic Fulgimides

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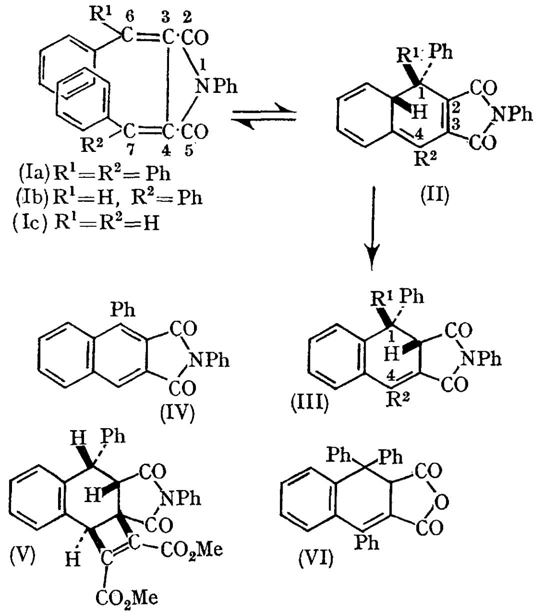
WE here use the name "fulgimides" for the novel class of compounds obtained by substitution of hydrogen in dimethylenesuccinimide, by analogy with the name "fulgides" assigned to the derivatives of dimethylenesuccinic anhydride.[1] Fulgimides with phenyl substituents in the 6- and 7-positions, like the corresponding fulgides, are bright yellow crystalline compounds which turn orange-red when exposed to ultraviolet light. The colour change can be reversed thermally or by exposure to a tungsten filament lamp. Fulgimides retain their photochromic properties in solution in organic solvents at room temperature, enabling quantitative studies on the spectroscopic and photochemical properties to be carried out more easily than on the fulgides which undergo rapid thermal reversal and side-reactions under similar conditions. The explanation by Santiago and Becker[2] for the structure of the photochrome formed on irradiation of fulgides has prompted us to communicate some supporting evidence from our work on fulgimides.

When the severely overcrowded compound, 1,6,6,7,7-pentaphenylfulgimide (Ia) in hexane at room temperature is exposed to radiation of wavelength 366 nm., the colour of the solution changes rapidly from yellow to orange-red. On prolonged irradiation, the solution became colourless and a quantitative yield of 1,2-dihydro-*N*-phenyl-1,1,4-triphenylnaphthalene-2,3-dicarboximide (IIIa) is obtained. We suggest that the red photochrome is the 1,8a-dihydronaphthalene derivative (IIa), formed by electrocyclic ring-closure of the fulgimide, that photochemical or thermal cleavage of the 1,8a carbon–carbon bond occurs readily to regenerate the fulgimide, and that the 1,2-dihydronaphthalene derivative (IIIa) is formed by a 1,5-shift of hydrogen in the photochrome (IIa). A similar mechanism for the photochemical rearrangement reactions of sterically hindered compounds has been suggested.[3] Santiago and Becker[2] have reported that no naphthalene derivative could be isolated after prolonged irradiation of 6,6,7,7-tetraphenylfulgide. We find that this fulgide undergoes a similar photo-rearrangement to that of pentaphenylfulgimide (Ia) to yield 1,2-dihydro-1,1,4-triphenylnaphthalene-2,3-dicarboxylic anhydride (VI).



N.m.r. studies have shown that arylidene- and diarylidene-succinic acids, obtained by the Stobbe condensation of aldehydes with succinic esters, have a *trans*-arrangement of aryl and carbonyl groups.[4] Fulgides and fulgimides, prepared from these acids retain the *trans*-arrangement. Isomers having a *cis*-configuration of aryl and carbonyl groups are not obtained by the Stobbe reaction, as has been stated by Brunow and Tylli,[5] Weinstein and his co-workers,[6] and implied in formulation by others.[2,7]

trans-1,6,6,7-Tetraphenylfulgimide (Ib) in hexane rearranges photochemically to *cis*-1,2-dihydro-*N*-phenyl-1,4-diphenylnaphthalene-2,3-dicarboximide (IIIb),[8] presumably through the red photochrome considered to be the 1,8a-dihydronaphthalene derivative (IIb). It is interesting that the identical dihydro-derivative (IIb) is obtained by thermal rearrangement of the fulgimide (Ib) at 200°. *trans,trans*-1,6,7-Triphenylfulgimide (Ic) also gives a red photochrome, and on prolonged irradiation in solution yields *N*-phenyl-1-phenylnaphthalene-2,3-dicarboximide (IV). *trans,trans*-6,7-Diphenylfulgide (VII) undergoes a similar reaction.[2,9] Irradiation of the fulgimide (Ic) in dimethyl acetylenedicarboxylate gives the adduct (V) of the dihydro-compound (IIIc). Thermal rearrangement of the fulgimide (Ic) by heating at 200° gives *cis*-1,2-dihydro-*N*-phenyl-1-phenylnaphthalene-2,3-dicarboximide (IIIc) which does not form an adduct when irradiated in dimethyl acetylenedicarboxylate. The structures of the compounds described follow from their n.m.r. spectra. All compounds gave satisfactory analysis.

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